

Short Communications

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Acta Cryst. (1969). B25, 988

Crystal data for 2,9-dimethyl-1,10-phenanthrolin. By DEB KUMAR SEN, *Physics Department, Presidency College, Calcutta 12, India*

(Received 23 July 1968)

2,9-Dimethyl-1,10-phenanthrolin is tetragonal, with $a=14.25$ and $c=22.15$ Å. The space group is $I4_1/a$.

As a part of our interest in compounds closely related to phenanthrene we have examined crystals of 2,9-dimethyl-1,10-phenanthrolin, $C_{14}H_{12}N_2$. Plate-like crystals of irregular hexagonal shape were produced by slow evaporation from a solution in ether at room temperature. Under a polarizing microscope one of the extinction directions was found to be parallel to one of the two longer edges of the crystal. Cell constants were determined from oscillation and Weissenberg photographs (zero and upper level) about the a and c axes, with Cu $K\alpha$ radiation. The density was measured by flotation.

Crystal data:

Tetragonal,

$a=b=14.25$ and $c=22.15$ Å;

sixteen formula units per unit cell.

$d_{calc}=1.23$ g.cm⁻³ and $d_{obs}=1.27$ g.cm⁻³.

Refractive indices: 1.65 along the c axis and 1.73 along the a and b axes.

Absent spectra:

$hkl : h+k+l \neq 2n$; $hk0 : h, (k) \neq 2n$ and $00l : l \neq 4n$.

Hence the space-group is $I4_1/a$.

No further work on this compound is contemplated.

The author would like to thank Dr B. S. Basak, Professor of Physics, Presidency College for his valuable assistance.

Acta Cryst. (1969). B25, 988

A refinement of the crystal structure of α'' -Cd₃As₂. By A. PIETRASZKO and K. ŁUKASZEWICZ, *Instytut Niskich Temperatur i Badań Strukturalnych Polskiej Akademii Nauk (Institute of Low Temperatures and Structure Research, Polish Academy of Sciences), Wrocław, Poland*

(Received 25 October 1968)

α'' -Cd₃As₂ which is stable in the temperature range 405–940°C can occasionally be obtained at room temperature. The crystal structure of α'' -Cd₃As₂ corresponds to that described by Stackelberg & Paulus (1935, *Z. phys. Chem.* B28, 427) for Cd₃As₂. Atomic parameters of α'' -Cd₃As₂ have been refined.

Pure cadmium arsenide undergoes a number of phase transitions at high temperatures (Węglowski & Łukaszewicz, 1968; Trzebiatowski, Królicki & Zdanowicz, 1968), forming the phases labelled α , α' , α'' and β . The crystal structure

of the room temperature form, α -Cd₃As₂, has been recently determined by Steigmann & Goodyear (1968). It was shown by Węglowski & Łukaszewicz (1968) that α'' -Cd₃As₂, stable in the temperature interval 405–940°C, has a lattice cell

Table 1. Atomic parameters

Origin at $\bar{4}m2$. Standard deviations are given in brackets.

| | Equipoint | x | y | z | B |
|-------|-----------|-------------|---------------|-------------|--------------------------|
| As(1) | 4(c) | 0 | 0 | 0.2494 (23) | 0.61 (60) Å ² |
| As(2) | 4(d) | 0 | $\frac{1}{2}$ | 0.2594 (38) | 0.51 (65) |
| As(3) | 8(f) | 0.2534 (15) | 0.2534 (15) | 0 | 0.77 (33) |
| Cd(1) | 8(g) | 0 | 0.2127 (20) | 0.1003 (12) | 0.61 (28) |
| Cd(2) | 8(g) | 0 | 0.2786 (21) | 0.3791 (15) | 1.51 (33) |
| Cd(3) | 8(g) | 0 | 0.2558 (30) | 0.6408 (16) | 2.61 (41) |

Table 2. *Observed and calculated structure factors*

Structure factors for non-observed reflexions are omitted. Reflexions indicated by an asterisk were not taken into account in the refinement.

| <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> _o | <i>F</i> _c | <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> _o | <i>F</i> _c | <i>h</i> | <i>k</i> | <i>l</i> | <i>F</i> _o | <i>F</i> _c |
|----------|----------|----------|-----------------------|-----------------------|----------|----------|----------|-----------------------|-----------------------|----------|----------|----------|-----------------------|-----------------------|
| 0 | 0 | 4 | 107 | 103 | 0 | 7 | 5 | 47 | 42 | 2 | 5 | 3 | 63 | 70 |
| 0 | 0 | 8 | 174 | 187 | 0 | 7 | 7 | 43 | 34 | 2 | 5 | 5 | 43 | 37 |
| 0 | 1 | 3 | 49 | 38 | 0 | 8 | 0 | 150 | 133 | 2 | 5 | 6 | 38 | 33 |
| 0 | 1 | 7 | 56 | 53 | 0 | 8 | 8 | 82 | 86 | 2 | 5 | 7 | 37 | 45 |
| 0 | 2 | 2 | 108 | 112 | 0 | 10 | 0 | 49 | 54 | 2 | 5 | 9 | 34 | 30 |
| 0 | 2 | 3 | 89 | 92 | 0 | 10 | 6 | 69 | 71 | 2 | 6 | 0 | 36 | 33 |
| 0 | 2 | 6 | 101 | 92 | 0 | 12 | 0 | 65 | 59 | 2 | 6 | 1 | 21 | 20 |
| 0 | 2 | 7 | 77 | 97 | 1 | 2 | 1 | 25 | 39 | 2 | 6 | 4 | 184 | 160 |
| 0 | 2 | 9 | 35 | 46 | 1 | 2 | 2 | 52 | 53 | 2 | 6 | 12 | 69 | 64 |
| 0 | 2 | 10 | 63 | 62 | 1 | 2 | 3 | 62 | 52 | 2 | 7 | 1 | 37 | 35 |
| 0 | 2 | 11 | 71 | 70 | 1 | 2 | 6 | 21 | 15 | 2 | 7 | 5 | 46 | 36 |
| 0 | 2 | 13 | 50 | 44 | 1 | 2 | 7 | 47 | 50 | 2 | 7 | 9 | 57 | 35 |
| 0 | 2 | 14 | 47 | 49 | 1 | 2 | 11 | 37 | 38 | 2 | 7 | 12 | 65 | 25 |
| 0 | 3 | 1 | 59 | 52 | 1 | 4 | 3 | 34 | 26 | 2 | 8 | 0 | 41 | 41 |
| 0 | 3 | 2 | 56 | 69 | 1 | 4 | 7 | 39 | 36 | 2 | 8 | 2 | 82 | 70 |
| 0 | 3 | 3 | 64 | 66 | 1 | 6 | 1 | 26 | 29 | 2 | 8 | 6 | 41 | 33 |
| 0 | 3 | 5 | 39 | 38 | 1 | 6 | 2 | 28 | 26 | 2 | 8 | 7 | 31 | 23 |
| 0 | 3 | 6 | 33 | 43 | 1 | 6 | 3 | 31 | 30 | 2 | 10 | 4 | 99 | 76 |
| 0 | 3 | 7 | 42 | 51 | 2 | 2 | 0 | 101 | 109 | 3 | 4 | 1 | 45 | 45 |
| 0 | 4 | 0* | 196 | 275 | 2 | 2 | 4* | 177 | 268 | 3 | 4 | 2 | 50 | 51 |
| 0 | 4 | 4 | 60 | 58 | 2 | 2 | 8 | 39 | 19 | 3 | 4 | 3 | 44 | 51 |
| 0 | 4 | 8 | 137 | 149 | 2 | 2 | 12 | 89 | 83 | 3 | 4 | 5 | 39 | 37 |
| 0 | 5 | 1 | 27 | 26 | 2 | 3 | 1 | 22 | 19 | 3 | 4 | 6 | 27 | 36 |
| 0 | 5 | 2 | 26 | 21 | 2 | 3 | 3 | 34 | 20 | 3 | 4 | 7 | 29 | 35 |
| 0 | 5 | 5 | 49 | 48 | 2 | 3 | 5 | 51 | 30 | 4 | 4 | 0* | 156 | 206 |
| 0 | 5 | 7 | 49 | 37 | 2 | 3 | 7 | 52 | 36 | 4 | 4 | 4 | 36 | 30 |
| 0 | 5 | 9 | 45 | 32 | 2 | 3 | 9 | 42 | 27 | 4 | 4 | 8 | 47 | 121 |
| 0 | 6 | 0 | 53 | 40 | 2 | 3 | 11 | 45 | 45 | 4 | 5 | 4 | 46 | 37 |
| 0 | 6 | 2 | 69 | 68 | 2 | 4 | 1 | 25 | 20 | 4 | 6 | 2 | 59 | 63 |
| 0 | 6 | 3 | 47 | 38 | 2 | 4 | 2 | 104 | 93 | 4 | 6 | 6 | 61 | 68 |
| 0 | 6 | 4 | 39 | 30 | 2 | 4 | 3 | 47 | 58 | 4 | 7 | 1 | 27 | 39 |
| 0 | 6 | 6 | 100 | 85 | 2 | 4 | 6 | 70 | 68 | 4 | 7 | 2 | 30 | 48 |
| 0 | 6 | 7 | 47 | 48 | 2 | 4 | 7 | 66 | 68 | 4 | 7 | 3 | 35 | 44 |
| 0 | 6 | 14 | 64 | 53 | 2 | 4 | 10 | 70 | 66 | 4 | 7 | 5 | 44 | 42 |
| 0 | 7 | 1 | 43 | 42 | 2 | 4 | 11 | 37 | 53 | 4 | 8 | 0 | 48 | 103 |
| 0 | 7 | 2 | 60 | 59 | 2 | 5 | 1 | 61 | 60 | 4 | 8 | 8 | 61 | 72 |
| 0 | 7 | 3 | 59 | 52 | 2 | 5 | 2 | 63 | 70 | | | | | |

corresponding to that determined by Stackelberg & Paulus (1935) for Cd₃As₂. It was also shown by Żdanowicz, Łukaszewicz & Trzebiatowski (1964) that this crystal structure can be easily stabilized by substituting a few per cent of cadmium by zinc. On the other hand, it has been reported (Węglowski & Łukaszewicz, 1968) that even in pure cadmium arsenide small acicular crystals with the lattice parameters of α''-Cd₃As₂ can occasionally be found among the ordinary α-Cd₃As₂ crystals. Although these crystals are in the metastable form (this was checked experimentally by Węglowski & Łukaszewicz, 1968), we assume that their structure does not differ significantly from that existing at temperatures between 405 and 940°C.

Small crystals with the α'' lattice cell were chosen from a sample of pure Cd₃As₂ obtained by sublimation. The lattice constants, $a = 8.963 \pm 0.004$, $c = 12.680 \pm 0.006$ Å, $c/a = 1.414$, agree well with the data of Stackelberg & Paulus (1935), $a = 8.958$, $c = 12.675$ Å, (converted from kX units). The space-group is $P4_2/nmc$ (No. 137), the unit cell containing 8 molecular units. The crystal used for intensity measurements was needle-like with dimensions $0.04 \times 0.04 \times 0.30$ mm, elongated parallel to the a axis of the unit cell. The intensity data were recorded with Zr-filtred Mo $K\alpha$ radiation on Weissenberg $0kl - 4kl$ photographs by the multiple-film technique. The intensities of 110 independent

Table 3. *Interatomic distances*

Standard deviations are less than 0.03 Å.

| | | | |
|--------------------|---------|-------------|---------|
| Tetrahedron Cd(1) | | As(1)-As(2) | 4.483 Å |
| | | As(1)-As(3) | 4.504 |
| Cd(1)-As(1) | 2.681 Å | As(1)-As(3) | 4.504 |
| Cd(1)-As(2) | 3.257 | As(2)-As(3) | 4.553 |
| Cd(1)-As(3) | 2.630 | As(2)-As(3) | 4.553 |
| Cd(1)-As(3) | 2.630 | As(3)-As(3) | 4.419 |
| Tetrahedron Cd(2) | | As(1)-As(2) | 4.483 |
| | | As(1)-As(3) | 4.461 |
| Cd(2)-As(1) | 3.008 | As(1)-As(3) | 4.461 |
| Cd(2)-As(2) | 2.505 | As(2)-As(3) | 4.413 |
| Cd(2)-As(3) | 2.702 | As(2)-As(3) | 4.413 |
| Cd(2)-As(3) | 2.702 | As(2)-As(3) | 4.419 |
| Tetrahedron Cd(3) | | As(1)-As(2) | 4.482 |
| | | As(1)-As(3) | 4.461 |
| Cd(3)-As(1) | 2.675 | As(1)-As(3) | 4.461 |
| Cd(3)-As(2) | 2.642 | As(2)-As(3) | 4.453 |
| Cd(3)-As(3) | 2.849 | As(2)-As(3) | 4.453 |
| Cd(3)-As(3) | 2.849 | As(3)-As(3) | 4.419 |
| Vacant tetrahedron | | As(2)-As(1) | 4.482 |
| | | As(2)-As(3) | 4.413 |
| | | As(2)-As(3) | 4.413 |
| | | As(3)-As(3) | 4.544 |
| | | As(3)-As(1) | 4.504 |
| | | As(3)-As(1) | 4.504 |

reflexions were estimated visually and corrected for Lorentz and polarization factors. No absorption corrections were applied.

The least-square refinement was started with the atomic parameters given by Stackelberg & Paulus (1935) for Zn_3P_2 . The calculations were performed on an Elliott 803 computer using a program (written by one of us, K.L.) with the diagonal approximation and isotropic temperature factors. The reflexions 040, 224 and 440, probably affected by extinction, were omitted. Atomic scattering factors for the neutral atoms Cd and As were taken from *International Tables for X-ray Crystallography* (1962) and corrected for anomalous scattering. After 10 cycles of refinement the R index (calculated for observed reflexions only) dropped from 0.24 to 0.138. Atomic parameters are given in Table 1, and the comparison of observed and calculated structure factors in Table 2. Interatomic distances, presented in Table 3, agree well with those given by Steigmann & Goodyear (1968) for Cd_3As_2 , which according to our notation should be named α - Cd_3As_2 .

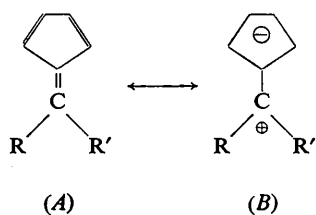
Acta Cryst. (1969). B25, 990

Zur Kristallographie der heterosubstituierten Fulvene. Von HANS BURZLAFF und REINHILD SALAMON, *Mineralogisches Institut der Universität Erlangen-Nürnberg* und KLAUS HARTKE und GERHILD SALAMON, *Institut für Pharmazeutische Chemie und Lebensmittelchemie, Marburg/L., Deutschland*

(Eingegangen am 17. September 1968)

The lattice parameters and the possible space groups for 12 different fulvenes are given; for three of them, structure determination has been started.

Heterosubstituierte Fulvene mit elektronenspendenden Substituenten R und R' (z. B. R = R' = Dialkylamino-, Alkylaryl-amino-, Alkoxy oder Alkylmercapto) haben im Laufe der letzten Jahre zunehmendes Interesse gefunden.



Im Vergleich mit den klassischen 6,6-Dialkyl- und 6,6-Diarylfulvenen (Bergmann, 1968) ist bei ihnen der Anteil der dipolaren Grenzform B am Grundzustand erheblich verstärkt. Spektroskopische Daten (NMR, IR und UV) sowie Dipolmomente erlauben die qualitative Aussage, dass der Bindungszustand der heterosubstituierten Fulvene eine Zwischenstellung einnimmt: Er lässt sich weder als typisch gekreuzt konjugiertes Doppelbindungssystem im Sinne der mesomeren Grenzform A noch als typisch nicht-benzoider aromatischer Carbocyclus im Sinne der mesomeren Grenzform B beschreiben.

A full discussion of phase transitions in the single composition Cd_3As_2 system will be possible after a determination of the crystal structure of α' Cd_3As_2 .

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Um bessere Vorstellungen über die Bindungsverhältnisse zu gewinnen, scheint es wünschenswert, möglichst genaue Winkel und Abstände zwischen den Atomen bei einigen Vertretern der heterosubstituierten Fulvene mit Hilfe einer Röntgenstrukturanalyse zu bestimmen, zumal ausser der Strukturuntersuchung am klassischen 6,6-Dimethylfulven (Norman & Post, 1961) bisher keine röntgenographischen Methoden angewendet worden sind.

Zur Vorbereitung der kristallographischen Strukturaufklärung wurden an einigen leicht zugänglichen Vertretern die Gitterkonstanten, das Zellvolumen V , die Auslöschungen auf Grund von Weissenberg- und Präzessionsaufnahmen und danach die möglichen Raumgruppen sowie die Röntgendichte D_R ermittelt. Die Ergebnisse dieser Untersuchungen sind in der Tabelle 1 zusammengestellt. Neben den erwähnten Daten findet man in der zweiten Spalte einen Literaturhinweis auf die Darstellung der betreffenden Substanz. In der vierten Spalte ist die experimentelle Dichte D_{exp} und das Dipolmoment Δ [Debye] zusätzlich angegeben, soweit sie gemessen wurden oder aus der Literatur bekannt sind.

Vom 6-Dimethylamino-6-morpholinofulven existieren zwei Phasen (a) und (b), die unter Nr. 3 und Nr. 4 in der Tabelle 1 aufgeführt sind.

Die Strukturaufklärung an den Substanzen Nr. 1, 5 und 12 (s. Tabelle 1) ist in Angriff genommen.